# Joining of Anodized and Stacked Aluminum Sheets by Copper Electrodeposition: Nano-Anchor Effect

AUTHOR(S):

Hakamada, Masataka; Kohashi, Yohei; Yamano, Yuriko; Mabuchi, Mamoru

CITATION:

Hakamada, Masataka ...[et al]. Joining of Anodized and Stacked Aluminum Sheets by Copper Electrodeposition: Nano-Anchor Effect. Materials Transactions 2018, 59(2): 324-326

ISSUE DATE:

2018-02-01

URL:

http://hdl.handle.net/2433/237644

*Materials Transactions*, Vol. 59, No. 2 (2018) pp. 324 to 326


**RAPID PUBLICATION**

# Joining of Anodized and Stacked Aluminum Sheets by Copper Electrodeposition: Nano-Anchor Effect

Masataka Hakamada, Yohei Kohashi[*1], Yuriko Yamano[*2] and Mamoru Mabuchi

*Department of Energy Science and Technology, Graduate School of Energy Science, Kyoto University, Kyoto 606–8501, Japan*

A new manufacturing process for metallic layers is proposed, where no thermal process is required. Al sheets were anodized in $H_3PO_4$, and the anodized sheets were adhered by Cu electrodeposition. The interface shear strength of Al/Cu was increased significantly from 1.5 to 64.8 MPa by the anodizing. Cu deposition in a small space between the Al sheets was important for the strong adhesion. Microstructural observation showed that Cu deposition penetrated the nanopores of an anodic aluminum oxide (AAO) film, which indicates that the nano-anchor effect played a critical role in the strong adhesion. [doi:10.2320/matertrans.M2017315]

(Received October 19, 2017; Accepted December 1, 2017; Published January 25, 2018)

***Keywords:*** *electrodeposition, metallic composites, anodic aluminum oxide*

## 1. Introduction

To date, many processes for manufacturing metallic dissimilar layers or laminates, *e.g.*, Al/Cu layers, have been developed, such as rolling followed by annealing[1)], friction stir welding (FSW)[2)], laser welding[3)], ultrasonic spot welding[4)], and explosive welding[5)]. In these processes, a thermal or diffusion process is required to bond the layers because bonding at room temperature is suppressed by the presence of rigid oxide films on the surfaces of metallic materials. However, thermal or diffusional processes often cause the formation of chemical compounds around the interfaces between dissimilar layers, which leads to premature fracturing or a reduced ductility[6)]. It is desirable to develop a new manufacturing process for metallic layers that exhibit an improved performance, without using a thermal process. Three mechanisms exist for the adhesion of metallic sheets: physical (diffusional) bonding, chemical bonding, and mechanical interlocking (anchor effect). Mechanical interlocking is an alternative for strongly adhering metallic sheets without thermal processes.

It is well known that an anodic aluminum oxide (AAO) film is formed by the electrochemical oxidation of aluminum. Masuda *et al.*[7)] showed that ordered nanohole arrays were formed by a two-step replication of the honeycomb structure of AAO. Since their discovery, many studies have been performed on ordered nanoporous AAO[8,9)]. Recently, it has been found that an electrodeposited Cu film adheres strongly to anodized Al[10,11)]. This occurs because the electrodeposited Cu is interlocked by the penetration of Cu into the nanopores of an AAO film. Thus, anodized Al sheets may be adhered strongly by Cu electrodeposition because of the nano-anchor effect. In this work, Al sheets were anodized and two anodized sheets were adhered by Cu electrodeposition (Fig. 1(a)). The adhesion strength (interface shear strength) was investigated by lap shear tests.

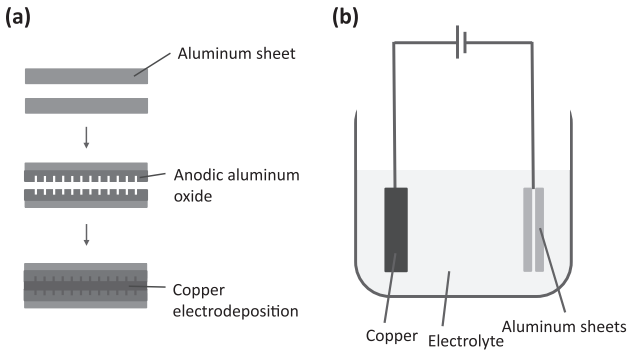


Fig. 1 (a) Schematic illustration of manufacturing process of an anodized Al sheet layer adhered by Cu electrodeposition. (b) Schematic illustration of Cu electrodeposition for adhering Al sheets.

## 2. Experimental

High-purity Al sheets that are 30 mm long, 4 mm wide, and 1.5 mm thick were used as starting materials. A surface of the Al sheet was polished to obtain a pentagonal cross section with an edge thickness of 1.4 mm, and the Al sheets were anodized under conditions where the electrolyte was 0.3 M $H_3PO_4$. The anodizing voltage was 30 V, and the anodizing conduction time was 40 min. A SUS316 sheet was used as a cathode in the anodizing treatment.

After the anodizing treatment, Cu electrodeposition was performed on the anodized Al sheets. The conditions for Cu electrodeposition are listed in Table 1. Two anodized sheets were laid with a space of 25 μm between them, so that the area for Cu electrodeposition was 20 mm × 4 mm. The Al sheet specimen, which consisted of two anodized Al sheets, was set as a cathode, a copper sheet was set as an anode in a sulfate bath, and Cu electroplating was carried out (Fig. 1(b)). Lap shear tests were conducted at room temperature on the Cu-electrodeposited Al sheet specimens to investigate the interface shear strength according to modified JIS K 6850[12)] with an overlap length of 20 mm and a sample width of 4 mm. Additional experiments were performed on Al sheets that were anodized in a 0.3 M $H_2CrO_4$ electrolyte, where the anodizing conditions were the same as those for anodizing treatment in 0.3 M $H_3PO_4$.

[*1]Graduate Student, Kyoto University. Present address: Canon Inc., Tokyo 146–8501, Japan
[*2]Graduate Student, Kyoto University

Table 1 Conditions for copper electrodeposition.

| | |
|---|---|
| Bath component | $CuSO_4 \cdot 5H_2O$ 220 g/L<br>$H_2SO_4$ 60 g/L<br>NaCl 0.1 g/L<br>Polyethyleneglycol 0.5 g/L |
| Bath volume | 250 mL |
| Current density | 1.875 A/dm$^2$ |
| Conduction time | 24 hours |
| Temperature | 298 K |
| Distance between electrodes | 5 cm |

## 3. Results and Discussion

Figure 2(a) shows an Al surface after anodizing in $H_3PO_4$. An AAO film with fine pores was formed by anodizing in $H_3PO_4$. An AAO film with fewer pores was formed by anodizing in $H_2CrO_4$ (Fig. 2(b)). The average pore diameter was 50.7 nm when anodizing with $H_3PO_4$ and 21.2 nm when anodizing with $H_2CrO_4$, and the porosity was 33.3% when anodizing with $H_3PO_4$ and 10.3% when anodizing with $H_2CrO_4$, where the pore diameter and porosity were calculated by image analyses on at least four observed images with an area of 12 μm × 10 μm. The pore formation was enhanced more by anodizing in $H_3PO_4$ than by anodizing in $H_2CrO_4$.

A 25-μm spacing is required between sheets to be filled with deposited Cu to ensure the adherence of the two Al sheets. To date, many studies[13–16] on Cu electrodeposition in small spaces have been carried out, and additives enable Cu electrodeposition in small spaces. In this work, a polyethyleneglycol (PEG) additive facilitated Cu electrodeposition in a small space between the two sheets. After the two Al sheets were adhered by the Cu electrodeposition, lap shear tests were carried out to investigate the interface shear strength of Al/Cu. Fracture occurred at the interface of the Al/Cu for the non-anodized Al sheet specimen and for the $H_2CrO_4$-anodized Al sheet specimen. The interface shear strength of Al/Cu was 1.5 MPa for the non-anodized Al sheet specimen and 4.3 MPa for the $H_2CrO_4$-anodized Al sheet specimen. For the $H_3PO_4$-anodized Al sheet specimen, fracture did not occur at the Al/Cu interface, but occurred inside the deposited Cu, as shown in Fig. 3. This result indicates that the interface shear strength of Al/Cu was higher than the shear strength of the deposited Cu. Additional lap shear tests, where only the contact area of Al/Cu was reduced to 1.5 mm × 1.2 mm, were performed on the $H_3PO_4$-anodized Al sheet specimen. As a result, fractures resulted at the Al/Cu interface and the interface shear strength was 64.8 MPa for the $H_3PO_4$-anodized Al sheet specimen. The interface shear strength was increased significantly from 1.5 to 64.8 MPa by anodizing in $H_3PO_4$.

A cross section of the Al sheet after the lap shear test is shown in Fig. 4 for the $H_3PO_4$-anodized Al sheets specimen. The deposited Cu penetrated the nanopores of an AAO film. The deposited Cu penetrated the nanopores of an AAO film less for the $H_2CrO_4$-anodized Al sheets specimen (Fig. 5). A significant increase in adhesion strength by the anodizing is related to the nano-anchor effect.

Figure 4(b) shows that Cu deposition penetrated the

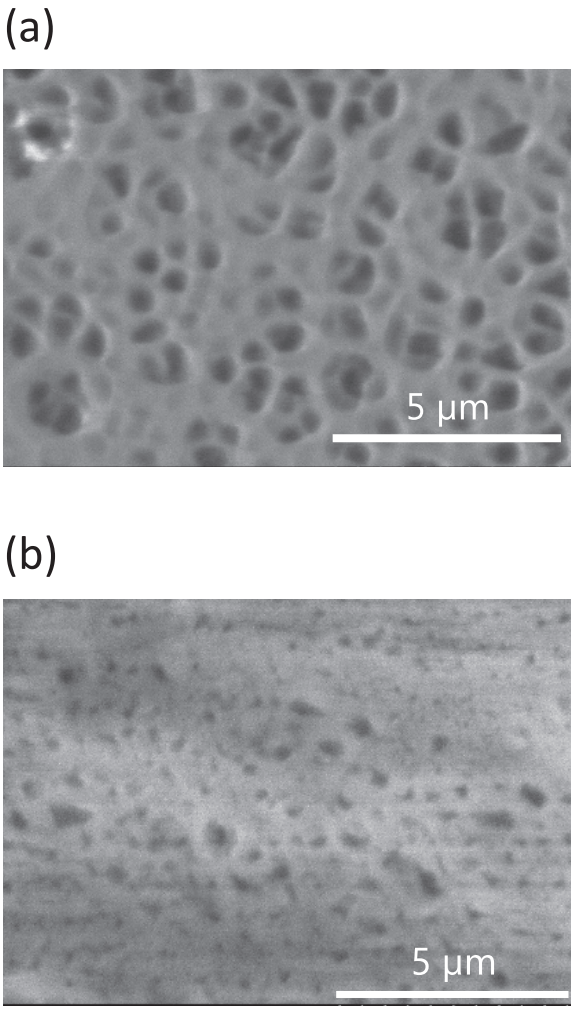


Fig. 2 Al surface after anodizing in (a) $H_3PO_4$ and (b) $H_2CrO_4$.

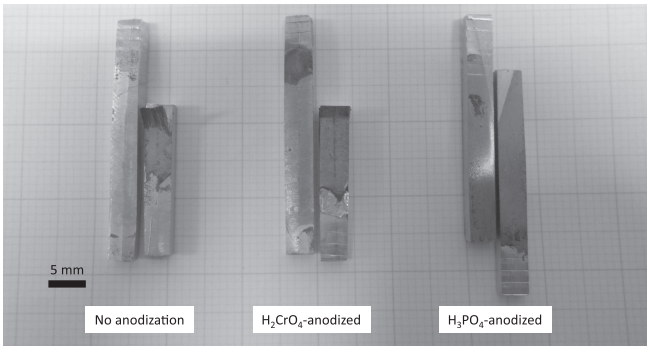


Fig. 3 Appearance of Al sheets after lap shear test. Sample without anodization and sample with $H_2CrO_4$ anodization showed fracture at Al/Cu interface (which can be judged by exposure of Al surface after shear test), while sample with $H_3PO_4$ anodization exhibited Cu/Cu fracture. Samples with no anodization and with $H_2CrO_4$-anodization are short because a part of the sample was cut off for cross sectional observation.

nanopores of an AAO film for the $H_3PO_4$-anodized Al sheet specimen. The Cu deposition branched off, as shown by circles in Fig. 3(b). Cu deposition branching did not result in the $H_2CrO_4$-anodized Al sheet specimen. For the $H_3PO_4$-anodized Al sheet specimen, more Cu deposition occurred in a cross section than expected by surface observation, as seen in the comparison between Fig. 2 and Fig. 3(a). This most

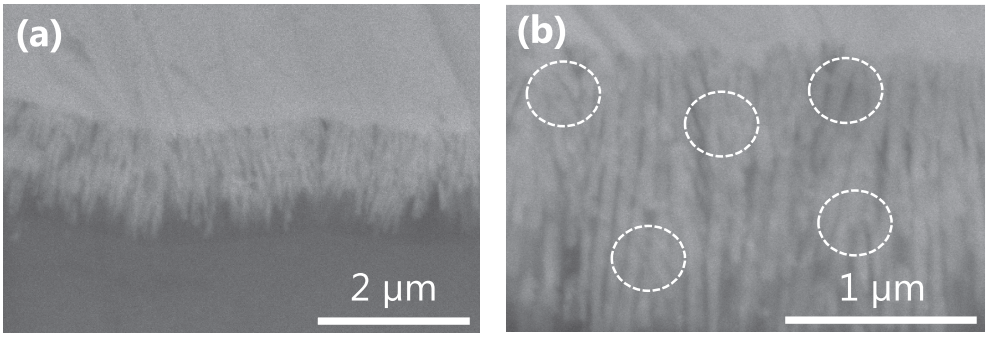


Fig. 4 Cross section of Al sheet after lap shear test for $H_3PO_4$-anodized Al sheet specimen observed with (a) low and (b) high magnification.

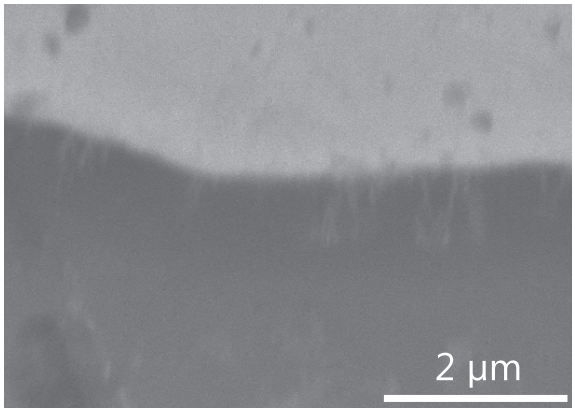


Fig. 5 Cross section of Al sheet after lap shear test for $H_2CrO_4$-anodized Al sheet specimen.

likely occurs because the pore diameter changed during pore growth.

This work shows that Al sheets were adhered strongly by Cu electrodeposition. One of the key points for the strong adhesion is Cu deposition in a small space between the Al sheets. In this work, PEG addition enabled Cu deposition in a small space. The other requirement for strong adhesion is the nano-anchor effect. As shown in Fig. 3(b), the Cu deposition branched off, which enhances the nano-anchor effect. The pore size was larger for the $H_3PO_4$-anodized Al sheet specimen than for the $H_2CrO_4$-anodized Al sheet specimen, which enables deep deposition of Cu into the nanopores and enhances the nano-anchor effect. However, if the pore size is too large, the adhesion strength will be reduced, as shown later. Thus, there may be an optimum pore size for strong adhesion. Also, additives such as PEG may play an important role in the deep penetration of Cu deposition into nanopores. A significant decrease in sample size leads to an enhanced strength[17]. Hence, the Cu deposition strength is expected to be increased by narrowing the Cu deposition that penetrates the nanopores. The nano-anchor effect may have been enhanced by these events.

## 4. Conclusions

Al sheets were anodized in $H_3PO_4$ and the anodized sheets were adhered by Cu electrodeposition. The interface shear strength of Al/Cu increased significantly from 1.5 to 64.8 MPa, by anodizing with $H_3PO_4$. A high Al/Cu adhesion strength (> 60 MPa) was obtained, which is attributed to the enhanced nano-anchor effect.

## Acknowledgements

M.H. thanks the Light Metal Educational Foundation, Inc., for financial support.

## REFERENCES

1) V. Yousefi Mehr, M.R. Toroghinejad and A. Rezaeian: Mater. Sci. Eng. A **601** (2014) 40–47.
2) A. Abdollah-Zadeh, T. Saeid and B. Sazgari: J. Alloy. Compd. **460** (2008) 535–538.
3) M.M. Hailat, A. Mian, Z.A. Chaudhury, G. Newaz, R. Patwa and H.J. Herfurth: Microsyst. Technol. **18** (2012) 103–112.
4) R. Balasundaram, V.K. Patel, S.D. Bhole and D.L. Chen: Mater. Sci. Eng. A **607** (2014) 277–286.
5) M.M. Hoseini Athar and B. Tolaminejad: Mater. Des. **86** (2015) 516–525.
6) C.-Y. Chen and W.-S. Hwang: Mater. Trans. **48** (2007) 1938–1947.
7) H. Masuda and K. Fukuda: Science **268** (1995) 1466–1468.
8) J. Martín, C.V. Manzano, O. C.-Calero and M. M.-González: ACS Appl. Mater. Interfaces **5** (2013) 72–79.
9) W. Lee, R. Ji, U. Gösele and K. Nielsch: Nat. Mater. **5** (2006) 741–747.
10) M.W. Losey, S.K. Griffiths and J.T. Hachman: J. Electrochem. Soc. **153** (2006) D177–D186.
11) I. Devyatkina, E.I. Yarovaya, V.V. Rogozhin, T.V. Markova and M.G. Mikhalenko: Russ. J. Appl. Chem. **87** (2014) 54–60.
12) Adhesives–Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies, JIS K 6850.
13) L. Bonou, M. Eyraud, R. Denoyel and Y. Massiani: Electrochim. Acta **47** (2002) 4139–4148.
14) J.-J. Sun, K. Kondo, T. Okamura, S.J. Oh, M. Tomisaka, H. Yonemura, M. Hoshino and K. Takahashi: J. Electrochem. Soc. **150** (2003) G355–G358.
15) K. Kondo, N. Yamakawa, Z. Tanaka and K. Hayashi: J. Electroanal. Chem. **559** (2003) 137–142.
16) J.W. Gallaway, M.J. Willey and A.C. West: J. Electrochem. Soc. **156** (2009) D287–D295.
17) M.D. Uchic, D.M. Dimiduk, J.N. Florando and W.D. Nix: Science **305** (2004) 986–989.